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A SUBDIVISION ALGORITHM FOR PHASE EQUILIBRIUM CALCULATIONS AT HIGH PRESSURES

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Abstract - Phase equilibrium calculations at high pressures have been a continuous challenge for scientists and engineers. Traditionally, this task has been performed by solving a system of nonlinear algebraic equations originating from isofugacity equations. The reliability and accuracy of the solutions are strongly dependent on the initial guess, especially due to the fact that the phase equilibrium problems frequently have multiple roots. This work is focused on the application of a subdivision algorithm for thermodynamic calculations at high pressures. The subdivision algorithm consists in the application of successive subdivisions at a given initial interval (rectangle) of variables and a systematic test to verify the existence of roots in each subinterval. If the interval checked passes in the test, then it is retained; otherwise it is discharged. The algorithm was applied for vapor-liquid, solid-fluid and solid-vapor-liquid equilibrium as well as for phase stability calculations for binary and multicomponent systems. The results show that the proposed algorithm was capable of finding all roots of all high-pressure thermodynamic problems investigated, independent of the initial guess used.

Keywords: Subdivision algorithm; Phase equilibrium; Phase stability; Thermodynamic modeling.

INTRODUCTION

The accurate prediction (calculation) of phase equilibrium of the fluid mixtures is an important aspect of many industrial applications, such as in the modeling, simulation and optimization of separation processes. In recent years, high-pressure operations under sub- or supercritical conditions have been considered as an alternative to conventional reaction and separation processes (Beckman, 2004; Arai et al., 2002; Marr and Gamse, 2000; Perrut, 2000; Fotouh and Shukla, 1996). Supercritical extraction of essential oil from herbaceous matrices, micro- and nano- particle formation, polymerization reactions under supercritical conditions, enzymatic reactions in supercritical solvents and essential oil fractionation are examples of these processes (Beckman, 2004; Perrut, 2000). For the development of any process at high pressures, an understanding of the phase behavior of the system, especially in the vicinity of the critical point, is of primary importance (Brennecke and Eckert, 1989). Thus, robust algorithms (routines) for phase equilibrium prediction (or calculations) are equally of great relevance.

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Fotouh and Shukla (1996) pointed out some difficulties in phase equilibrium calculation at high pressures: first, the number of phases in equilibrium must be known a priori and second, close to the critical locus of the mixture, the calculation strongly depends on the initial values of the unknown variables in the numerical method used, often resulting in trivial solutions (phases in equilibrium with identical compositions).

The phase equilibrium can be modeled using two approaches: i) the minimization of the total Gibbs free energy and ii) the solution of a nonlinear algebraic system. The first approach is based on the fact that at fixed T and P, the condition that is necessary and sufficient for a multi-component and multi-phase system to reach equilibrium is the minimum of the total Gibbs free energy. Thus, the phase and chemical equilibrium problem can be formulated and solved as a global optimization problem (Sofyan et al., 2003; Nichita et al., 2002; Rangaiah, 2001). Likewise, the Helmoholtz free energy can be minimized at fixed T and V (total molar volume) (Souza et al., 2006). The second approach consists in solving a system of nonlinear equations obtained from the equations of mass balance and phase equilibrium (isofugacity equations for all components in the mixture for all phases in equilibrium) (Bausa and Marquardt, 2000; Sum and Seader, 1995).

The development of approaches to solve the phase equilibrium problem has been the subject of continuous investigation in the scientific literature. Most of the work has considered the application of Newton's based methods, where the initial guesses for unknown variables have a direct influence on the success of finding a solution to the problem. A major difficulty of this method is seen when the system of equations has multiple solutions. Some recent work in the literature uses strategies that minimize the dependence on the initial guess or approaches that seek all roots of the algebraic system independent of the initial guess. Of these, the following can be cited: multigrid mesh initialization (Sofyan et al., 2003), the homotopy continuation method (Bausa and Marquardt, 2000; McDonald and Floudas, 1995; Seider et al., 1991; Kuno and Seader, 1988; Wayburn and Seader, 1987) and the interval analysis algorithms – applied to flash and phase stability analysis problems (Scurto et al., 2003; Kerfott et al., 1994; Hua et al., 1998a,b; Kerfott and Novoa, 1990).

The homotopy continuation method (Kuno and Seader, 1988; Wayburn and Seader, 1987) is an interesting algorithm for phase equilibrium calculations, since according to the authors, it is possible to find all roots (solutions) of the problem. However, implementation of this method is not a simple task and previous knowledge of the problem is necessary to determine the homotopy type that should be adopted - fixed point, Newton's homotopy or affine homotopy. The performance and success of this method in finding all possible solutions (roots) are directly associated with the choice of homotopy type (Wayburn and Seader, 1987).

Smiley and Chun (2001) recently presented a subdivision algorithm with exclusion to locate all roots of a nonlinear algebraic system, where the authors present a section proofing the convergence for the subdivision algorithm. In general, subdivision algorithms consist in establishing initial intervals for the system variables and then a systematically subdividing these intervals. At each division level, it is necessary to apply a test to verify the existence of roots. If this interval passes the test, it is retained and it continues as part of the procedure; otherwise it is discarded. After a finite number of subdivisions, a conventional and local method (like the Newton-Raphson or Broydn method), in which the midpoint of the retained intervals can be used as initial guess is used to find the roots. Thus, depending on the number of subdivisions applied, the solution (or solutions) can be closed in the retained intervals, which can provide a fast, efficient and safe convergence of the conventional method. It should be mentioned that the subdivision algorithm can also be employed as a preprocessor algorithm to generate approximates initial guess in the conventional and local methods.

Recently, Boynd (2006a,b) presented some applications of the subdivision algorithm for computing real roots of polynomial equations. However, to the best of our knowledge, no application of the subdivision algorithm to phase equilibria or chemical engineering problems is available in the literature.

Considering the little readiness of algorithms that are characterized by easy implementation and manipulation, robustness and the capability of locating multiple solutions (roots), the aim of this present work is to investigate the application of an algorithm, denominated subdivision algorithm (SubDivNL), for phase equilibrium calculations at high pressures. The main idea of the proposed algorithm is based on the work presented by Smiley and Chun (2001).

SUBDIVISION ALGORITHM

Considering a system of nonlinear algebraic equations, $\mathbf{F}(\mathbf{x})$, in accordance with Smiley and Chun (2001), the basic idea of the proposed subdivision algorithm is as follows: given an initial interval for unknown variables ("rectangle") $R \in \Re^d$, to find all values of **x**, such that $\mathbf{x}^* = \left\{\mathbf{x} \in \Re^d : \mathbf{F}(\mathbf{x}) = \mathbf{0}\right\}$, from successive subdivision of *R*, where *d* is the dimension of the problem. In the *R* subdivision procedure, a partition sequence is needed. This can be done by partitioning *R* into two equal parts for each coordinate (variable); thus, for a rectangle at $\Re^d$, there will be 2^d new subrectangles. *R* can stand for the "parent" rectangle and the congruent subrectangles (originating from division of *R*) the "child" rectangles. At each subdivision level "*i*", there will be R_{ij} child subrectangles, where "*j*" are the subrectangles generated.

For each subrectangle R_{ij} generated, a test to verify the existence of solutions is applied as expressed in Equation 1. If the subrectangle R_{ij} passes the test, it is retained (saved) and will be a new "parent" rectangle, which in turn will divide at $i = i + 1$. In the present work, the following selection criterion was used to test the existence of solution in a rectangle:

If

$$\left\|\mathbf{F}(\mathbf{x}_{ij})\right\| \le 2^{-i} + \tau_{ij}; \tag{1}$$

then R_{ij} is retained; otherwise it is discarded.

where

$$\tau_{ij} = \frac{1}{2}\sum_{k=1}^{d}\left(\max_{y \in R_{ij}}\left\|\frac{\partial \mathbf{F}(\mathbf{x})}{\partial y_k}\right\|_2\right)\left|b_k - a_k\right|$$

and a_k and b_k are the lower and upper bounds of the R_{ij} rectangle with dimension"*k*" and **y** is the vector of random sampled points in R_{ij} with dimension "*k*". In order to obtain the coordinates for each "child" rectangle, the following scheme is proposed in this work:

$$\begin{cases} a_k = A_k + \boldsymbol{\alpha}_{m,d} v_k \\ b_k = a_k + v_k \end{cases} \quad m = 1,\ldots,2^d;\; k = 1,\ldots,d \tag{2}$$

where

$$v_k = \frac{1}{2}(B_k - A_k) \qquad k = 1,\ldots,d \tag{3}$$

where $\boldsymbol{\alpha}_{m,d}$ is a matrix of elements 0 (zero) and 1 (one) combined in such a way that, in each iteration "*i*" it is moved in the coordinates of "child" rectangles. A_k and B_k are the lower and upper bounds of parent rectangles for each variable "*k*", respectively; v_k is the midpoint coordinate of the parent rectangles of variable "*k*" and a_k and b_k are the lower and upper coordinates of the new child rectangle for the variable "*k*".

In this work, the sample number (*iRan*) was specified as *iRan* = 5xd (Smiley and Chun, 2001 proposed use of *iRan* = 5). In Figure 1 a scheme of the subdivision algorithm proposed in this work is shown.

The SubDivNL subdivision algorithm was used to solve distinct thermodynamic problems at high pressures, consisting of nonlinear algebraic equation systems – phase equilibrium calculations and phase stability analysis. The problems tested were separated into two sections: phase stability test problems and phase equilibrium calculations. For each type of problem, a brief description of the approach employed is presented. The thermophysical properties used in this work are presented in Table 1. For the naphthalene, fusion temperature, $T_f = 353.45$ K; fusion enthalpy, $\Delta H_f = 19318.3976$ J/mol; subcooled liquid molar volume, $V_S = 131.2$ (cm^3/mol); and solid molar volume, $V_S = 111.94$ (cm^3/mol), were used in accordance with Corazza et al. (2004). The Peng-Robinson equation of state (PR-EoS) (Peng and Robinson, 1976) with quadratic mixing rules at two parameters (vdW2) was used to model the fluid phases in equilibrium. The calculations were done on a personal microcomputer Intel Pentium IV with 2.66 GHz and 512 MB of RAM. No further code optimization, like code parallelization, was performed in the present work.

```
i)    Given $d$, $A_k$ and $B_k$ $(k=1,..,d)$, iRan, iMax, $\mathbf{F}(\mathbf{x})$, iCov
ii)   Set $M = 1$ (initialize with a "parent" rectangle)
iii)  For $l=1,...,iCov$ do:
      a. For $i=1,...,iMax$ do:
            i.   Set $m = 0$
            ii.  For $j=1,...,M*2^d$ do:
                   1. Apply equations (5) and (6) to obtain the coordinate
                      for each $R_{ij}$ "child" rectangle
                   2. Get iRan random samples in $R_{i,j}$
                   3. Evaluate $\left\|\mathbf{F}(\mathbf{x}_{ij})\right\|$ for each random number in $R_{ij}$
                   4. Evaluate $\tau_{ij}$ (equation 4)
                   5. If $\left\|\mathbf{F}(\mathbf{x}_{ij})\right\| \le 2^{-i} + \tau_{ij}$, then
                        a. Retain the $R_{i,j}$ rectangle
                        b. Set $m = m + 1$
                   6. else discard it
            iii. Set $M = m$
      b. Evaluate the adjacent rectangles (coverage)
      c. Reset $M$ ($M$ = number of new rectangles)
iv)   Use the Newton method to find $\mathbf{x}^* = \left\{\mathbf{x} \in \mathbb{R}^d : \mathbf{F}(\mathbf{x}) = 0\right\}$, applying the
      midpoint of each $R_{i,j}$ as initial guess
v)    Check the solutions (roots) found
vi)   Show all solutions (roots)
```

Figure 1: The subdivision algorithm implemented (SubDivNL). *iRan*: random sample number for each rectangle R_{ij}; *iMax*: maximum subdivision number (or level); *iCov*: maximum coverage number; and *M*: number of rectangles retained at each subdivision level.

Table 1: Thermophysical properties of pure components (Reid et al., 1988).

Component	Tc [K]	Pc [bar]	ω
carbon dioxide	304.21	73.83	0.2236
propane	369.80	41.90	0.0152
n-pentane	469.70	33.69	0.2514
ethanol	513.92	61.48	0.6444
trans-2-hexen-1-ol [a]	601.76	36.73	0.7240
methane	190.60	46.00	0.0080
hydrogen sulfide	373.20	89.40	0.1000
water	674.30	220.50	0.3440
dichloromethane	510.00	63.00	0.1990
limonene	657.16	27.56	0.3396
nitrogen	126.20	33.90	0.0400
ethane	305.40	48.80	0.0980
naphthalene [b]	748.40	40.50	0.3020

[a] Stradi et al. (2001), [b] Corazza et al. (2004).

APPLICATION OF SUBDIVNL TO PHASE STABILITY TEST

Problem Formulation

A sufficient condition for equilibrium at specified temperature (T), pressure (P) and global composition (**z**) is that the Gibbs surface tangent plane distance should be nonnegative for all possible phases in the system (Balogh et al., 2003; Rangaiah, 2001; Hua et al., 1998b; Baker et al., 1982). The Gibbs surface tangent plane distance function (*TPD*) can be given by

$$\mathrm{TPD}(\mathbf{y}) = \sum_{k}^{nc} y_k \left(\mu_k(\mathbf{y}) - \mu_k(\mathbf{z})\right) \tag{4}$$

$$\text{s.t.} \sum_{k}^{nc} y_k = 1 \quad 0 \le y_k \le 1$$

where *nc* is the number of components in the mixture and μ_k represents the chemical potential of component *k*. The solution of equation (4) refers to stationary points of *TPD* as a function of **y** and the global solution corresponds to a global minimum of Gibbs free energy. Adopting the isofugacity approach to model the fluid phases in equilibrium, from equation (4)

$$\mathrm{TPD}(\mathbf{y}) = \sum_{k}^{nc} y_k \left\{ \ln(\hat{\phi}_k y_k) - \ln(\hat{\phi}_k^* z_k) \right\} \tag{5}$$

$$\text{s.t.} \sum_{k}^{nc} y_k = 1 \quad 0 \le y_k \le 1$$

where $\hat{\phi}_k$ and $\hat{\phi}_k^*$ are the fugacity coefficients of component "*k*" for new tried and tested phases, respectively, and y_k and z_k are the compositions of new (tried) and tested phases, respectively. As the solutions of equation (5) are stationary points, the system can be solved by differentiating with respect to y_k in order to obtain the following system of nonlinear algebraic equations:

$$\left\{ \ln(y_k \hat{\phi}_k) - \ln(z_k \hat{\phi}_k^*) \right\} -$$

$$\left\{ \ln(y_{nc} \hat{\phi}_{nc}) - \ln(z_{nc} \hat{\phi}_{nc}^*) \right\} = 0 \ ; \ k = 1, \ldots, nc-1 \tag{6}$$

$$\sum_{k}^{nc} y_k = 1$$

In order to test the subdivision algorithm for phase stability analysis, binary, ternary and quaternary systems were selected from the literature. Systems were chosen for being well described and also due to their noneasy numerical solution.

CO_2(1) + Trans-2-Hexen-1-ol(2) Binary System

After preliminary tests, the subdivision level *i* was fixed equal to 6, *iCov* = 0 (noncoverage was applied). The initial interval of composition (mole fraction) for all components, **y,** was set as [0.0, 1.0]. The phase stability analysis results obtained for the CO_2(1) + trans-2-hexen-1-ol(2) system are presented in Table 2. The binary interaction parameters for the PR-EoS were $k_{12} = 0.084$ and $l_{12} = 0.0$ (Stradi et al., 2001).

The roots found, the Euclidian norm of the system and the values of the *TPD* function for each specified condition (input) are presented in Table 2. It should be observed in this table that the results found with the SubDivNL algorithm are in agreement with the ones presented in the literature (Hua et al., 1999), where interval analysis was used (IN/GB algorithm). In this table the CPU time for all solutions of each calculation condition is also presented and it can be observed that, besides the algorithm's ability to find all roots, a very short CPU time is required for the calculations. An observation of Table 2 reveals that for the third condition, the fifth root presented in the literature (0.9968) was not found in this work. This is due to the kind of formulation of the phase equilibrium problem. In our algorithm, we selected one root of the equation of state, depending on the type of phase tested. In interval analysis the equation of state is part of the nonlinear algebraic system and volume is one of the unknowns in the problem.

Table 2: Phase stability analysis for the CO_2 (1) + trans-2-hexen-1-ol (2) binary system using the SubDivNL algorithm and results from the literature.

Input (P [bar]; T[K]; z_1)	SubDivNL				IN/GB (Hua et al., 1999)	
	Roots Found (x_1)	$\lVert F(x) \rVert$	TPD – SubDivNL	CPU [s]	Roots Found (x_1)	TPD - INGB
(120.00, 303.15, 0.8500)	1. (0.7651)	0.26×10^{-7}	-4.0081×10^{-4}	4.69×10^{-2}	1. (0.7645)	-4.1×10^{-4}
	2. (0.8500)	0.47×10^{-8}	-8.3086×10^{-15}		2. (0.8500)	0.0
	3. (0.9198)	0.11×10^{-7}	-4.6057×10^{-4}		3. (0.9200)	-4.7×10^{-4}
(80.00, 303.15, 0.8500)	1. (0.7082)	0.72×10^{-8}	-2.5379×10^{-3}	6.20×10^{-2}	1. (0.7078)	-0.003
	2. (0.8500)	0.51×10^{-7}	-5.5816×10^{-14}		2. (0.8500)	0.0
	3. (0.9600)	0.71×10^{-7}	-3.9596×10^{-3}		3. (0.9600)	-0.004
(69.7016, 303.15, 0.9991)	1. (0.6979)	0.67×10^{-7}	-6.4569×10^{-4}	6.25×10^{-2}	1. (0.7018)	3.6×10^{-4}
	2. (0.8468)	0.87×10^{-8}	2.4546×10^{-3}		2. (0.8428)	0.0030
	3. (0.9723)	0.82×10^{-7}	-4.3204×10^{-3}		3. (0.9728)	-0.004
	4. (0.9991)	0.60×10^{-8}	1.7740×10^{-12}		4. (0.9991)	0.0
					5. (0.9968)	0.0020

N_2(1)+CH_4(2)+Ethane(3) and CH_4 (1)+CO_2(2)+H_2S(3) Ternary Systems

As mentioned above for the binary system investigated, the subdivision level *i* was fixed equal to 6 and *iCov* = 0 (noncoverage was applied). The initial interval of composition (mole fraction) for all components, **y**, was specified as [0.0, 1.0]. For the N_2(1)+CH_4(2)+ethane(3) ternary system, the binary interaction parameters for PR-EoS were k_{12}=0.038, l_{12}=0.0, k_{13}= 0.080, l_{13}=0.0, k_{23}=0.021 and l_{23}=0.0 (Sofyan et al., 2003; Hua et al., 1998a). For the CH_4(1)+CO_2(2)+H_2S(3) ternary system, the binary interaction parameters for PR-EoS were k_{12} = 0.1005, l_{12} = 0.0, k_{13} = 0.0755, l_{13} = 0.0, k_{23} = 0.0999 and l_{23} = 0.0 (Sofyan et al., 2003).

Tables 3 and 4 contain the results of the phase stability analysis for the N_2(1)+CH_4(2)+ethane(3) and CH_4(1)+CO_2(2)+H_2S(3) ternary systems, respectively. In these tables the Euclidian norm of the algebraic systems, along with the *TPD* values for each root found at the stationary point in the *TPD* function, are also presented. In all cases it should be noted that the results of the SubDivNL algorithm are in agreement with those presented in the literature where interval analysis was used to find the roots.

Table 3: Phase stability analysis for the N_2(1)+CH_4(2)+ethane (3) ternary system using the SubDivNL algorithm and results from the literature.

Input (P [bar]; T[K]; z_1; z_2)	SubDivNL				IN/GB (Hua et al., 1998a)	
	Roots Found (x_1, x_2)	$\|F(x)\|$	TPD - SubDivNL	CPU [s]	Roots Found (x_1, x_2)	TPD – IN/GB
(76.00, 270.00, 0.3000, 0.1000)	1. (0.1330, 0.0678)	0.14×10^{-6}	-1.4830×10^{-2}	0.41	1. (0.1330; 0.0680)	-0.0148
	2. (0.3000, 0.1000)	0.99×10^{-7}	1.4006×10^{-15}		2. (0.3000; 0.1000)	0.0
	3. (0.3117, 0.1016)	0.98×10^{-7}	-5.8889×10^{-6}		3. (0.3120; 0.1020)	-5.8×10^{-6}
(76.00, 270.00, 0.1500, 0.3000)	1. (0.0968, 0.2451)	0.47×10^{-7}	-1.1746×10^{-3}	0.80	(0.1470; 0.2970)	3.55×10^{-7}
	2. (0.1470, 0.2974)	0.35×10^{-7}	3.3979×10^{-7}		(0.0970; 0.2450)	-0.0012
	3. (0.1500, 0.3000)	0.34×10^{-7}	2.1507×10^{-16}		(0.1500; 0.3000)	0.0
(76.00, 270.00, 0.080, 0.3800)	1. (0.0800, 0.3800)	0.38×10^{-7}	-1.3900×10^{-15}	0.50	(0.080; 0.380)	0.0

Table 4: Phase stability analysis for the methane(1)+CO_2(2)+hydrogen sulfide(3) ternary system using the SubDivNL algorithm and results from the literature.

Input (P [bar]; T[K]; z_1; z_2)	SubDivNL				IN/GB (Hua, 1997)	
	Roots Found (x_1, x_2)	$\|F(x)\|$	TPD - SubDivNL	CPU [s]	Roots Found (x_1, x_2)	TPD – IN/GB
(55.10, 208.5, 0.4989, 0.0988)	1. (0.2779, 0.0953)	0.95×10^{-7}	-3.7072×10^{-3}	32.0	1. (0.2450, 0.0910)	-6.8×10^{-3}
	2. (0.4989, 0.0988)	0.10×10^{-6}	-3.8421×10^{-15}		2. (0.4990, 0.099)	0.0
	3. (0.7813, 0.0664)	0.20×10^{-6}	-5.9477×10^{-3}		3. (0.8170, 0.0600)	-9.7×10^{-3}
	4. (0.8631, 0.0488)	0.29×10^{-6}	-4.5856×10^{-3}		4. (0.8590, 0.0510)	-9.4×10^{-3}
	5. (0.9159, 0.0347)	0.51×10^{-6}	-9.1584×10^{-3}		5. (0.9190, 0.034)	-0.015
(48.60, 227.55, 0.4989, 0.0988)	1. (0.3004, 0.0969)	0.96×10^{-7}	-3.5258×10^{-3}	40.4	1. (0.2780, 0.094)	3.55×10^{-7}
	2. (0.4989, 0.0988)	0.11×10^{-6}	-3.3877×10^{-15}		2. (0.4990, 0.0990)	0.0
	3. (0.8969, 0.0412)	0.42×10^{-6}	-0.1811		3. (0.9000, 0.0410)	-0.1850

CH_4(1)+CO_2(2)+H_2S(3)+Water(4) Quaternary System

For this system, the binary interaction parameters for the PR-EoS were k_{12}=0.1005, l_{12}=0.0, k_{13}=0.0755, l_{13}=0.0, k_{14}=0.4928, l_{14}=0.0, k_{23}=0.0999, l_{23}=0.0, k_{24}=0.0, l_{24}=0.0, k_{34}=0.0400 and l_{34}=0.0 (Sofyan et al., 2003). Table 5 contains the results obtained in the phase stability analysis, where it can be observed that the results of the SubDivNL algorithm are in agreement with those presented in the literature. It should also be observed that the CPU time for the quaternary system was slightly longer than that obtained for the ternary systems, but is of the same order as the CPU time obtained by Sofyan et al. (2003), who employed a tunneling algorithm for the calculations.

Table 5: Phase stability analysis for the methane(1)+CO_2(2)+hydrogen sulfide(3)+water(4) quaternary system using the SubDivNL algorithm and results from the literature.

Input (P [bar]; T[K]; z_1; z_2, z_3)	SubDivNL				IN/GB (Hua, 1997)	
	Roots Found (x_1, x_2, x_3)	$\lVert F(x) \rVert$	TPD - SubDivNL	CPU [s]	Roots Found (x_1, x_2, x_3)	TPD – IN/GB
(181.70, 449.85, 0.0496, 0.0494, 0.4000)	1. (0.0496,0.0494, 0.4000)	0.89×10^{-7}	-1.0747×10^{-15}	147.05	1. (0.0500, 0.0500, 0.4000)	0.0
	2. (3.586×10^{-4}, 3.785×10^{-3}, 0.0448)	0.29×10^{-6}	-0.1736		2. (3.5×10^{-4}, 0.0040, 0.0450)	-0.1759
	3. (0.4007, 0.0968, 0.4158)	0.16×10^{-6}	-0.2989		3. (0.3990, 0.0970, 0.4170)	-0.2948
(76.00, 310.95, 0.1488, 0.2991, 0.0494)	1. (0.9644, 0.0330, 0.002395)	0.78×10^{-4}	-0.0272	57.89	1. (0.9650, 0.0330, 0.0020)	-0.0271
	2. (0.1488, 0.2991, 0.0494)	0.37×10^{-7}	-9.0285×10^{-15}		2. (0.1490, 0.2990, 0.0490)	0.0
	3. (0.2669×10^{-5}, 0.7169×10^{-3}, 0.2353×10^{-3})	0.48×10^{-6}	-0.0118		3. (2.7×10^{-6}, 7.2×10^{-4}, 2.4×10^{-4})	-0.0117

APPLICATION OF SUBDIVNL FOR PHASE EQUILIBRIUM PROBLEMS AT HIGH PRESSURES

Thermodynamic Modeling Formulation Using the Symmetric Approach

The use of the isofugacity formulation (symmetric approach) to model the phase equilibrium problem results in a system of nonlinear equations,

$$\hat{f}_k^L - \hat{f}_k^V = 0 \quad k = 1,..,nc \tag{7}$$

If a solid phase is present in the mixture,

$$\hat{f}_{0,nc}^S - \hat{f}_k^\zeta = 0 \quad k = 1,..,nc \tag{8}$$

In equations (7) and (8), the fugacity of vapor and liquid phases are $\hat{f}_k^V = y_k \hat{\phi}_k^V P$ (*k = 1,...,nc)* and $\hat{f}_k^L = x_k \hat{\phi}_k^L P$ (*k = 1,...,nc)*, respectively. The superscript ζ in (8) can refer to a vapor or a liquid phase. When a solid phase was present, it was considered a pure phase and the fugacity of subcooled liquid ($f_{nc,0}^{LSC}$) was calculated in accordance with Corazza et al. (2004), Diefenbacher and Turk (2002) and Kikic et al. (1997).

Additionally, the mass balance constraints to components in the phases in equilibrium must be observed

$$(\sum_{k=1}^{nc} y_k = 1 \text{ and } \sum_{k=1}^{nc} x_k = 1).$$

The Peng-Robinson cubic equation of state (PR-EoS - Peng and Robinson, 1976) with van der Waals quadratic mixing rules at two parameters (k_{ij} and l_{ij}) was employed to model the fluid phases (vapor and liquid). Typical phase equilibrium problems (bubble and dew points and flash calculations) were selected to test the ability of the proposed subdivision SubDivNL algorithm.

Bubble-T and Dew-T Calculations for the CO_2(1)+Propane(2) Binary System

The binary parameters used for this system were k_{12}=0.1676 and l_{12}=0.0752 (Corazza et al., 2003). At specified T (temperature) and **x** (known phase composition), the initial interval for this system was chosen as [1.0, 100.0] bar for pressure (P) and [0.0, 1.0] for the unknown phase composition (**y**). The maximum subdivision parameter was specified as *iMax* = 8. After the subdivision procedure, the Newton method was used for each rectangle retained. The results are presented in Table 6, which also shows the performance of the direct application of the Newton method (using the mnewt routine as presented by Press et al., 1992) for distinct initial guesses. It should be noted from this table that the Newton method converges to distinct roots depending on the initial guess, while the SubDivNL algorithm was initialized in wide pressure and molar composition ranges: from 1.0 to 100.0 bar and from 0.0 to 1.0, respectively.

The results presented in Table 6 provide evidence of the importance of robust methods to find all phase equilibrium solutions independent of the initial guess. This aspect is even more important in the parameter estimation of the thermodynamic models, where phase equilibrium calculations (bubble points, dew points or flash calculations) are conducted several times for each experimental point. Indeed, as the thermodynamic models are usually sensitive to variations in interaction parameters, a small change can produce infeasible convergence and consequently hinder and jeopardize the truthfulness of the results.

Table 6: Bubble-P calculations with the Subdivision Algorithm (SubDivNL) and the mnewt routine (Press et al., 1992) for the CO_2(1)+propane(2) binary system.

SubDivNL algorithm		mnewt algorithm	
Input (T [K], x_1)	**Roots Found (P [bar], y_1)**	**Initial Guess (P [bar], y_1)**	**Roots Found (P [bar], y_1)**
(311, 0.05)	1. (112.81, 0.0500)* 2. (18.28, 0.1793)	1. (50.0, 0.90) 2. (50.0, 0.10) 3. (50.0, 0.30) 4. (20.0, 0.30)	1. (18.28, 0.1793) 2. (59.65, 0.050)* 3. (104.75, 0.050)* 4. (18.28, 0.1793)
(311, 0.50)	1. (115.67, 0.5000)* 2. (30.94, 0.2228) 3. (50.64, 0.6952)	1. (150.0, 0.90) 2. (30.0, 0.90) 3. (40.0, 0.10)	1. (121.90, 0.50)* 2. (50.64, 0.6952) 3. (30.94, 0.2228)
(311, 0.75)	1. (100.89, 0.7500)* 2. (60.06, 0.6458) 3. (66.29, 0.7778)	1. (50.0, 0.30) 2. (40.0, 0.95) 3. (80.0, 0.95) 4. (1.0, 0.10)	1. (60.06, 0.6458) 2. (32.98, 0.7500)* 3. (66.29, 0.7775) 4. (1.56, 0.7500)*

* Trivial Solutions.

Bubble-P and Flash Calculations for the n-Pentane(1)+Ethanol(2) Binary System

Figure 2 depicts a phase diagram for this system at 422.6 K. All bubble point calculations were performed with the SubDivNL algorithm with *iMax* = 8 and initial intervals of [1.0, 100.0] bar for pressure and [0.0, 1.0] for n-pentane mole fraction. The binary interaction parameters used for the PR-EoS were k_{12} = 0.1210 and l_{12}= 0.0 (Orbey and Sandler, 1998). It can be observed in this figure that the SubDivNL algorithm was shown to be efficient, even with the occurrence of an azeotropic point (mathematical singularity ($\mathbf{x} = \mathbf{y}$)), where most of the conventional methods have difficulty converging to this point.

The use of flash calculations in phase equilibrium problems with closed phase compositions presents some difficulty of convergence. The SubDivNL algorithm was applied to the flash calculation for the n-pentane(1)+ethanol(2) system at 422.6 K, 17.70 bar and 0.8300 of n-pentane mole fraction (see Figure 2). The interval used for mole fraction of the liquid and vapor phases was [0.0, 1.0] for both components. The results of this calculation are presented in Table 7. The CPU time was 0.10 s. In Table 7 it can be verified that the algorithm was able to simultaneously find both roots for this problem, the unfeasible solution (solution *1* in Table 7) and the true solution (solution *2* in Table 7). The true solution (stable from stability test) can be qualitatively verified in Figure 2.

Table 7: Flash calculation for the n-pentane(1)+ethanol(2) system with the SubDivNL algorithm.

Input (T [K], P[bar], z_1)	**Roots Found (x_1, y_1)**	$\lVert \mathbf{F}(\mathbf{x}) \rVert$	**Vapor Phase Fraction**
(422.6, 17.70, 0.8300)	1^a. (0.2667, 0.4689) 2. (0.8578, 0.8099)	$0.1854\text{x}10^{-6}$ $0.8321\text{x}10^{-7}$	-1.7867 0.4192

^{a}Unfeasible Solution

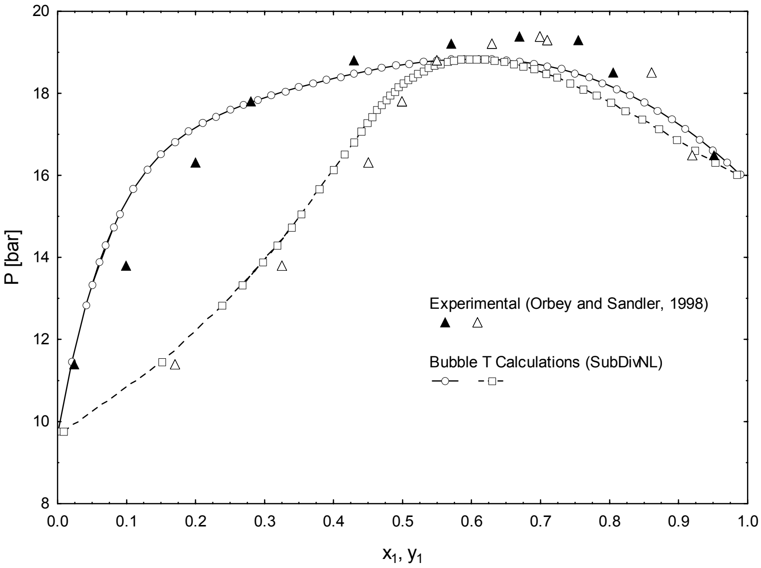

Figure 2: Diagram of pressure composition for the n-pentane(1)+ethanol(2) binary system at 422.6 K.

Bubble-P Calculations for the CO_2(1)+ Dichloromethane(2)+Limonene(3) Ternary System

The binary interaction parameters used for this system were $k_{12} = 0.0940$, $l_{12} = -0.0281$, $k_{13} = 0.0296$, $l_{13} = -0.00661$, $k_{23} = 0.0$ and $l_{23} = 0.0$ (Corazza et al., 2003a). The maximum subdivision level for the SubDivNL algorithm was *iMax* = 8. The specified variables (inputs) along with the results obtained are presented in Table 8. The initial interval for the dependent variables was [1.0, 300.0] bar for pressure and [0.0, 1.0] for mole fraction of components (1) and (2). It should be noted that the PR-EoS was capable of predicting the phase behavior of the ternary system from binary system information (Corazza et al., 2003b). Also, the SubDivNL algorithm proposed converged for all system roots, including the trivial solutions for all calculations.

Table 8: Bubble-P calculations for the CO_2(1)+dichloromethane(2)+ limonene(3) ternary system using the SubDivNL algorithm.

Specified Variables (T [K], z_1, z_2)	Roots Found (P [bar], y_1, y_2)	$\|F(x)\|$
(313, 0.8731, 0.0884) ^{C1}	1. (74.74, 0.9912, $0.2321\text{x}10^{-2}$) 2. (130.20, 0.8731, 0.0884)*	$0.16\text{x}10^{-6}$ $0.54\text{x}10^{-8}$
(313, 0.7537, 0.0457) ^{C2}	1. (71.63, 0.9928, 0.0019) 2. (88.0, 0.7537, 0.0457)*	$0.30\text{x}10^{-7}$ $0.23\text{x}10^{-7}$
(313, 0.6269, 0.2072) ^{C3}	1. (58.49, 0.9858, 0.0008) 2. (91.52, 0.6269, 0.2072)*	$0.70\text{x}10^{-7}$ $0.55\text{x}10^{-8}$
(333, 0.7537, 0.0457) ^{C4}	1. (100.15, 0.9798, 0.0093) 2. (130.20, .0.7537, 0.0457)*	$0.11\text{x}10^{-7}$ $0.31\text{x}10^{-10}$
(333, 0.6269, 0.2072) ^{C5}	1. (79.25, 0.9738, 0.0026) 2. (89.00, 0.6269, 0.2072)*	$0.41\text{x}10^{-7}$ $0.55\text{x}10^{-8}$

*Trivial Solution; Pressure values of experimental points (Corazza et al. 2003b):
C1 = 75.92 bar; C2 =72.19 bar; C3 = 58.49 bar ; C4 = 100.92 bar; C5 = 86.75 bar.

Solid-Fluid Equilibrium Calculations for the CO_2(1)+Naphthalene(2) Binary System

The binary interaction parameters for PR-EoS were k_{12}=0.0793 and l_{12}=-0.0357, and the solid naphthalene properties were used in accordance with Corazza et al. (2004). The S-F calculations were performed for T=338.05 K and P=120 bar, for which the initial coordinates for the unknown variable (y_2) were [0.0, 1.0]. The results presented in Table 9 indicate that for this problem also the subdivision SubDivNL algorithm was efficient in locating all roots of the problem independently of the initial estimative.

Table 9: S-F equilibrium calculations for the CO_2(1)+naphthalene(2) binary system.

Input Variable (T [K], P [bar])	Output variable (y_2, y_1)	$\|F(x)\|$
(338.05, 120.0)	1. (0.0047, 0.9953)	$7.0x10^{-7}$
	2. (0.1122, 0.8878)	$1.1x10^{-7}$
	3. (0.5466, 0.4534)*	$3.5x10^{-8}$
(338.05, 150.0)	1. (0.0203, 0.9797)	$5.2x10^{-7}$
	2. (0.0921, 0.9079)	$6.4x10^{-7}$
	3. (0.5092, 0.4908)*	$2.9x10^{-8}$

* Stable Solution

S-V-L Equilibrium Calculation for the CO_2(1)+Naphthalene(2) Binary System

For this three-phase binary system, at a given temperature, the problem consists in finding the composition of the vapor and liquid phases (**x** and **y**, respectively) and the pressure (P) of the system. For this problem, the coordinates of the initial rectangle for the unknown variables were [0.0, 1.0] for CO_2 mole fraction in vapor and liquid phases and [1.0, 200.0] for pressure. The results obtained are presented in Table 10, where it can be verified that the algorithm was efficient in locating solutions for these calculations. It should be noted that this problem has a high degree of numerical difficulty, mainly related to initialization of the calculations, which once again confirms the robustness of the SubDivNL algorithm.

Table 10: S-V-L equilibrium calculations for the CO_2(1)+naphthalene(2) binary system.

Input T [bar]	Roots Found (P [bar], y_1, y_2, x_1, x_2)	$\|F(x)\|$
338.05	(96.45, 0.9982, 0.0012, 0.4169, 0.5831)	$2.5x10^{-6}$
345.00	(52.88, 0.9993, 0.0004, 0.2127, 0.7873)	$5.3x10^{-6}$

CONCLUSIONS

In this work the application of a subdivision algorithm (SubDivNL) for thermodynamic calculations at high pressures was proposed. The subdivision algorithm consists in applying successive subdivisions at a given initial interval (rectangle) of variables and systematically testing to verify the existence of roots in each one. If the interval checked passes the test, then it is retained; otherwise it is discharged. Two main categories of problems were considered for binary and multicomponent systems: the phase stability problem and the phase equilibrium calculation, involving bubble and dew points and flash calculations. The results show that it was possible to obtain the solution (root) or multiple solutions (roots) of the system independent of the initial guess, which is an important advantage over conventional methods, like Newton-based methods (it should be remembered that for composition the initial interval used was 0.0 to 1.0 in all cases investigated). The success in resolving different types of problems on phase equilibrium indicates the potentiality and robustness of the proposed algorithm in thermodynamic calculations at high pressures.

NOMENCLATURE

d	problem dimension
f(x)	nonlinear equation
$\mathbf{F(x)}$	system of nonlinear equations
$\hat{f}_k^F$	fugacity of component “k” in phase “F” in the mixture
R	multidimensional rectangle
a_k	lower coordinate of the “child” rectangles in dimension “*k*”
b_k	upper coordinate of the “child” rectangles in dimension “*k*”
A_k	lower coordinate of the “parent” rectangles in dimension“*k*”
B_k	upper coordinate of the “parent” rectangles in dimension “*k*”
i	subdivision level
$\mathbf{y}$	vector of random point in R_{ij} and vapor phase mole fraction
$\mathbf{x}_{ij}$	middle point of rectangle “j” at subdivision

	level “i”’
x	liquid phase mole fraction
z	global mole composition
P	total pressure
P_c	critical pressure
T	temperature
T_c	critical temperature
iRan	sample number in R_{ij}
iMax	maximum subdivision number
iCov	maximum coverage number

Greek Letters

ν_k	coordinate of the midpoint of the “parent” rectangle at “k” dimension
$\hat{\phi}_k^F$	fugacity coefficient of component “k” in phase “F” in the mixture
τ_{ij}	subdivision parameter of rectangle “j” at the subdivision level “i”
$\alpha_{m,n}$	matrix of zero and one elements
ω	acentric factor

Subscripts

0	pure component
nc	number of components in the mixture and n^{th} components of the system

Superscripts

LSC	subcooled liquid
V	vapor phase
L	liquid phase
S	solid phase

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REFERENCES

Arai, Y., Sako, T. and Takebayashi, Y., Supercritical Fluids: Molecular Interactions, Physical Properties, and New Applications. Springer, Germany, 2002.

Baker, L.E., Pierce, A.C. and Luks, K.D., Soc. Petrol. Engrs. J., 22, 731 (1982).

Balogh, J., Csendes, T. and Stateva, R.P., Application of a Stochastic Method to the Solution of the Phase Stability Problem: Cubic Equations of State, Fluid Phase Equilibria, 212, 257 (2003).

Bausa, J. and Marquardt, W., Quick and Reliable Phase Stability Test in VLLE Flash Calculations by Homotopy Continuation, Computational Chem. Eng., 24, 2447 (2000).

Beckman, E.J., Supercritical and Near-critical CO_2 in Green Chemical Synthesis and Processing, J. Supercrit. Fluids, 28, 121 (2004).

Boynd, J.P., Computing Real Roots of a Polynomial in Chebyshev Series Form through Subdivision with Linear Testing and Cubic Solves. Applied Math. and Computation, 174, 1642 (2006a).

Boynd, J. P., Computing real Roots of a Polynomial in Chebyshev Series Form through Subdivision. Applied Numerical Math., 56, 1077 (2006b).

Brennecke, J.F. and Eckert, C.A., AIChE. J., 35, 1409 (1989).

Corazza, M.L., Cardozo Filho, L., Antunes, O.A.C. and Dariva, C., High Pressure Phase Equilibria of the Related Substances in the Limonene Oxidation in Supercritical CO2, Chem. Eng. Data, 48, 354 (2003a).

Corazza, M.L., Cardozo Filho, L., Antunes, O.A.C. and Dariva, C., Phase Behavior of the Reaction Medium of Limonene Oxidation in Supercritical Carbon Dioxide, Ind. Eng. Chem. Res., 42, 3150 (2003b).

Corazza, M.L., Cardozo Filho, L. and Dariva, C., SLV Equilibrium for CO_2+Co-solvent+solute System: Experimental Data and Modeling, In: V Brazilian Meeting on Supercritical Fluids, Florianópolis-SC, Brazil (2003).

Corazza, M.L., Cardozo Filho, L., Oliveira, J.V. and Dariva, C., A Robust Strategy for SLV Equilibrium Calculations at High Pressures, Fluid Phase Equilibria, 221, 113 (2004).

Diefenbacher, A.E. and Türk, M., Phase Equilibria of Organic Solid Solutes and Supercritical Fluids with Respect to the RESS Process, J. Supercritical Fluids, 22, 175 (2002).

Fotouh, K. and Shukla, K., Comparative Study of Numerical Methods for Calculating Phase Equilibria in Fluid Mixtures from an Equation of State, Chem. Eng. Science, 51, 3763 (1996).

Hua, J.Z., Interval Method for Reliable Computations of Phase Equilibrium from Equation of State Models. Ph.D. Dissertation, University of Illinois, Urbana-Champaign, IL, 1997, cited by Y. Sofyan, A.J. Ghajar and A.M. Gasem., Ind. Eng. Chem. Res., 42, 3786 (2003).

Hua, J.Z., Brennecke, J.F. and Stadtherr, M.A., Enhanced Interval Analysis for Phase Stability: Cubic Equation of State Models, Ind. Eng. Chem. Res., 37, 1519 (1998a).

Hua, J.Z., Brennecke, J.F. and Stadtherr, M.A., Reliable Computation of Phase Stability Using Interval Analysis: Cubic Equation of State Models, Comput. Chem. Eng., 22, 1207 (1998b).

Hua, J.Z., Maier, R.W., Tessier, S.R., Brennecke, F. and Stadtherr, M.A., Interval Analysis for Thermodynamic Calculations in Process Design: A Novel and Completely Reliable Approach, Fluid Phase Equilibria, 158-160, 607 (1999).

Kerfott, R.B., Dawande, M., Du, K.-S. and Hu, C.-Y, Algorithm 737: INTLIB, a Portable Fortran 77 Interval Standard Function Library, ACM Trans. Math. Software, 20, 447 (1994).

Kerfott, R.B. and Novoa, M., Algorithm 681: INTBIS, a Portable Interval Newton/Bisection Package, ACM Trans. Math. Software, 16, 152 (1990).

Kikic, I., Lora, M. and Bertucco, A., A Thermodynamic Analysis of Three-Phase Equilibria in Binary and Ternary Systems for Applications in Rapid Expansion of a Supercritical Solution (RESS), Particles from Gas-Saturated Solutions (PGSS), and Supercritical Antisolvent (SAS), Ind. Eng. Chem. Res. 36, 5507 (1997).

Kuno, M. and Seader, J.D., Computing All Real Solutions to Systems of Nonlinear Equations with a Global Fixed-point Homotopy, Ind. Eng. Chem. Res., 27, 1320 (1988).

Marr, R. and Gamse, UT., Use of Supercritical Fluids for Different Processes Including New Developments—A Review, Chem. Eng. and Processing, 39, 18 (2000).

McDonald, C. and Floudas, C.A., Global Optimization for the Phase Stability Problem, AIChE Journal, 41, 1798 (1995).

Nichita, D.V., Gomez, S. and Luna, E., Multiphase Equilibria Calculation by Direct Minimization of Gibbs Free Energy with a Global Optimization Method, Computers and Chem. Engineering, 26, 1703 (2002).

Orbey, H. and Sandler, S.I., Modeling Vapor-Liquid Equilibria: Cubic Equations of State and Their Mixing Rules, Cambridge University Press, Cambridge (1998).

Peng, D.Y. and Robinson, D.B., A New Two-Constant Equation of State, Ind. Eng. Chem. Fundam., 15, 59 (1976).

Perrut, M., Supercritical Fluid Applications: Industrial Developments and Economic Issues, Ind. Eng. Chem. Res., 39, 4531 (2000).

Press, W.H., Teukolsky, S.A., Vetterling, W.T. and Flannery, B.P., Numerical Recipes in FORTRAN: The Art of Scientific Computing, Second Edition, Cambridge University Press, Cambridge (1992).

Rangaiah¸ G.P., Evaluation of Genetic Algorithms and Simulated Annealing for Phase Equilibrium and Stability Problems, Fluid Phase Equilibria, 187-188, 83 (2001).

Reid, R.C., Prausnitz, J.M. and Poling, B.E., The Properties of Gases & Liquids, McGraw-Hill, Fourth Edition, NY (1988).

Scurto, A.M., Xu, G., Brennecke, J.F. and Stadtherr, M.A., Phase Behavior and Reliable Computation of High-Pressure Solid-Fluid Equilibrium with Cosolvents, Ind. Eng. Chem. Res., 42, 6464 (2003).

Seider, W.D., Brengel, D.D. and Widagdo, S., Nonlinear Analysis in Process Design, AIChE Journal, 37, 1 (1991).

Smiley, M.W. and Chun, C.J., An Algorithm for Finding All Solutions of a Nonlinear System, Computational and Applied Math., 137, 293 (2001).

Sofyan, Y., Ghajar, A.J. and Gasem, A.M., Multiphase Equilibrium Using Gibbs Immunization Techniques, Ind. Eng. Chem. Res., 42, 3786 (2003).

Souza, A.T., Cardozo-Filho, L., Wolff, F. and Guirardello, R., Application of Interval Analysis for Gibbs and Helmoholtz Free Energy Global Minimization in Phase Stability Analysis, Brazilian J. Chem. Eng., 23, 117 (2006).

Stradi, B.A., Stadtherr, M.A. and Brennecke, J.F., Multicomponent Phase Equilibrium Measurements and Modeling for the Allylic Epoxidation of *trans*-2-hexen-1-ol to (2R,3R)-(_)-3-propyloxiranemethanol in High-pressure Carbon Dioxide, J. Supercritical Fluids, 20, 1 (2001).

Sum, A.C. and Seider, W.D., Homotopy-continuation Method for Stability Analysis in the Global Minimization of the Gibbs Free Energy, Fluid Phase Equilibria, 103, 203 (1995).

Wayburn, T.L. and Seader, J.D., Homotopy Continuation Method for Computer-Aided Process Design, Comput. Chem. Eng., 11, 7 (1987).